

COMPOSITE STRUCTURAL MATERIAL AND
METHOD OF MAKING SAME

BACKGROUND OF THE INVENTION

There are many different structural materials made at least in part from synthetic resins, that are intended to be used in place of wood. An elusive goal in designing such materials is the combination of reasonable cost with relatively high strength and stiffness. Thus, for example, synthetic lumber made by hot melt extrusion of mixtures of waste wood fiber and recycled thermoplastic material such as polyethelene can be produced at a low enough cost to make them feasible for use as decking boards. Such synthetic lumber is generally considered unsuitable, however, for uses that require it to withstand higher bending and compression loads, require increased static strength and stiffness requirements, and/or require greater shock and impact resistance. Thus, it is generally unsuitable for use as primary structural load-bearing elements, such as posts, joists, beams, and stringers for shipping pallets. For those types of uses a material has to have a higher flexural modulus of rupture, izod impact resistance, ultimate compressive strength, Young's modulus, and/or accelerating weight resistance than are found in the hot melt extrudates of polymer and wood particles.

As a result of extensive experimentation, the present inventors have discovered a type of design for a composite structural material that can be manufactured economically, yet have a relatively high flexural modulus of rupture, izod impact resistance, ultimate compressive strength, Young's modulus, and accelerating weight impact resistance. Also, if desired, relatively light weight materials can be used, so that the composite can have a specific gravity approaching that of some species of wood that are used for lumber.

-2-

SUMMARY OF THE INVENTION

The composite structural material of the present invention comprises a dimensionally stable core material ensheathed in a dimensionally stable, laminar covering that is adherent to the core material. The laminar covering is comprised of at least one band of substantially parallel reinforcing cords bonded to at least one layer of a dimensionally stable web material selected from the group consisting of rigidified paper and rigidified cloth.

5

10

15

20

The core material can be any dimensionally stable solid. Rigid as well as semi-rigid solids can be used. (By "rigid" is meant herein at least substantially rigid.) As examples of rigid solids, wood itself can be used as the core material, as can gypsum and Portland cement compositions, e.g., cement that is mixed (diluted) with cellulose fiber. In the semi-rigid category are elastomers, e.g., natural or synthetic rubber. Preferably the core has sufficient crush resistance that it will transfer a load (stress) on one surface of the composite to the opposite surface thereof. I.e., if the top surface is put under a compressive load the bottom surface will be placed under tension, due to the core's resistance to crushing.

Whether rigid or semi-rigid, the core material is preferably comprised of a resin. For some applications the core material preferably is comprised of pieces of a filler solid embedded in a resinous matrix. (The term "resinous matrix," as used herein, is intended to embrace both filled and unfilled resins.) Because the laminar covering is dimensionally stable, it functions rather like an exoskeleton in the composite structural material of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

THE RESINOUS MATRIX

25

When the core material comprises a resinous matrix, preferably it is a thermosetting resin. Examples of suitable thermosetting resins include epoxy resins, urea-formaldehyde resins, melamine-formaldehyde resins, phenol-formaldehyde resins, polyester resins, and polyurethane resins (both polyether-polyurethanes and polyester-polyurethanes).

-3-

5

10

15

20

25

When it is important that the structural material have as low a specific gravity as is reasonably possible, it is preferred that the resinous matrix be a foamed synthetic resin, most preferably a rigid or semi-rigid polyurethane or phenolic foam. Polyurethane resins are made by reacting polyols with polyisocyanates. The reaction is exothermic. Cross-linking, or branching, of the polyurethane molecules can be achieved by including in the reaction mixture some polyol molecules and/or isocyanate molecules that have at least three functional groups, and by adjusting the ratio of reactants accordingly. With sufficient cross-linking, rigid or semi-rigid thermoset polymers are obtained. The degree of rigidity can be controlled, for example, by the choice of polyol that is used, which is well-known in the art.

To make rigid or semi-rigid polyurethane foam, a mixture is made of a polyfunctional isocyanate, a polyol, a blowing agent, a catalyst, and, usually, a cell-size regulator (e.g., a surfactant). A urethane-forming reaction begins once the ingredients are combined. An exotherm forms, and the blowing agent or agents cause closed cells to form in the polymer as the mass expands and solidifies. The exotherm typically reaches a peak temperature of at least about 150° F. The isocyanate and polyol reactants include enough molecules with three or more functional groups that the degree of cross-linking or branching is sufficient to produce at least a semi-rigid foam.

Aromatic polyisocyanates often are used when making rigid or semi-rigid foam. Some examples are toluene diisocyanate (TDI) and polymeric isocyanate (PMDI), which is obtained by the condensation of aniline with formaldehyde.

Polyols that can be used include polyether polyols and polyester polyols. Propylene oxide adducts of polyfunctional hydroxy compounds or amines are one type of polyether polyol that can be used. Mixtures of polyester polyols and polyether polyols sometimes are employed.

Halogenated hydrocarbons, such as hydrochlorofluorocarbons and hydrofluorocarbons, can be used as blowing agents. Lower alkanes such as

-4-

butanes, pentanes, and cyclopentanes can be used as well. Liquid carbon dioxide can be used. Water can also be used, as it will react with isocyanate to generate carbon dioxide in situ. Sometimes water or carbodiimide catalysts are used to generate carbon dioxide as a co-blown agent. Often the blowing agent or agents are preblended with the polyol, together with the catalyst and the cell-size regulator, which usually is a surfactant.

All of this is well known to persons of ordinary skill in the art and is described, for example, in Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. (1997), vol. 24, pp. 695-715, which is incorporated herein by reference.

The term "polyurethane system" can be used to refer to a particular combination of isocyanate, polyol, catalyst, blowing agent, and cell size regulator that is capable of reacting to form a polyurethane foam. A characteristic that helps identify and distinguish polyurethane systems is the density of the foam a particular system will create when the components are mixed in an open vessel (the "free rise density"). It is thought that polyurethane systems capable of yielding a free rise density of about 3 or 4 pcf to about 35 pcf are generally preferred for use in the present invention, most preferably those capable of yielding a free rise density of about 4 to about 20 or 25 pcf.

Examples of some commercial isocyanate/polyol pairings that can be employed in forming polyurethane systems for use in the present invention are the following:

<u>Isocyanate Component</u>	<u>Polyol Component</u>	<u>Rated Free Rise Density (pcf)</u>
Rubinate M	Rimline WL 87380	8-9
Rubinate M	Rimline WL 87381	15-18
Baydur 645 B	Baydur 645 A	5
Baydur 730 B (U 731 B)	Baydur 649 A	9

-5-

In the above table, the Rubinate and Rimline reactants are available from Huntsman Chemicals, and the Baydur reactants are available from Bayer Corporation.

5 Phenolic foams can be made, for example, from resole resins, e.g., phenol-formaldehyde resins made from a molar excess of formaldehyde. The preparation of such a foam is disclosed, for example, in U.S. Patent No. 5,653,923 to Spoo et al., which is incorporated herein by reference.

THE FILLER SOLID

10 The filler solid, when used, preferably comprises pieces of one or more of the following: lignocellulosic material, cellulosic material, vitreous material, cementitious material, carbonaceous material, plastic, and rubber.

Cellulosic and Lignocellulosic Fillers

15 Suitable lignocellulosic materials include wood, e.g., wood powder, wood flake, and waste wood fiber, as well as fiber from woody plants. Suitable cellulosic materials include, for example, plant material such as bamboo, palm fiber, bagasse, rice straw, rice hulls, wheat straw chaff, hemp, sisal, corncobs, and seed shells, e.g., walnut shells. If lignocellulosic or cellulosic material is used, preferably it is fibrous.

Vitreous Fillers

20 Suitable vitreous materials include glass (including volcanic glass), fly ash, and ceramic particles. Vitreous spheres can be used, e.g., glass or ceramic microspheres, the weight majority of which have a diameter of about 5 to 225 microns. To lighten the weight, such microspheres can be hollow. Specific examples include Z-Light® ceramic microspheres, which are available from 3M Company and which have a bulk density of approximately 0.7 g/cc and a crush strength of about 2,000 to 3,500 psi. These come in different versions. One version that it is believed may be especially suitable is Z-Light W-1020 microspheres, the weight majority of which have diameters in the range of about 25 10 to 120 microns and a crush strength of approximately 3,500 psi.

-6-

Among the various hollow glass microspheres that can be used are Scotchlite® Glass Bubbles, also from 3M Company, e.g., Scotchlite 538, which has a bulk density of about 0.38 g/cc, a crush strength of about 4,000 psi, and particle sizes that mostly (as measured by weight, not the number of microspheres) fall in the range of about 8 to 88 microns.

Where a filler having a relatively high specific gravity can be used, as, for example, where a savings in the cost of raw materials is a greater priority than keeping down the weight of the composite, solid glass microspheres, which are relatively inexpensive, can be used.

When used, glass microspheres might constitute, for example about 2 to 90 percent of the volume of the finished material's core.

Perlite is often preferred as a vitreous filler, especially when expanded to form a lightweight aggregate. When used, expanded perlite might constitute, for example, about 10 to 80 percent of the volume of the finished material's core.

Glass or ceramic reinforcing fibers also can be used.

Cementitious Fillers

As suitable cementitious material may be mentioned, for example, Portland cement, gypsum, blast furnace cement, silica cement, and alumina cement.

Carbonaceous Fillers

As suitable carbonaceous material may be mentioned, for example, carbon black and graphite, as well as carbon fibers.

Plastic Fillers

As regards plastic materials, both thermoset and thermoplastic resins can be used. As suitable plastics may be mentioned, for example, addition polymers (e.g., polymers of ethylenically unsaturated monomers), polyesters, polyurethanes, aramid resins, acetal resins, phenol-formaldehyde resins, melamine-formaldehyde resins, and urea-formaldehyde resins. Homopolymers and copolymers can be used. Suitable copolymers include interpolymers, graft copolymers, and block copolymers.

-7-

As examples of suitable addition polymers may be mentioned polyolefins, polystyrene, and vinyl polymers. Suitable polyolefins include, for example, those prepared from olefin monomers having two to ten carbon atoms, e.g., ethylene, propylene, butylene, and dicyclopentadiene. Poly(vinyl chloride) and acrylonitrile polymers can be used. Particles of waste plastic, e.g., post-consumer waste plastic such as used plastic bags and containers, can be used. Examples include bottles made of high density polyethylene and polyethylene grocery store bags.

As suitable polyesters may be mentioned polymers formed by condensation reaction of one or more polycarboxylic acids with one or more polyhydric compounds, e.g., an alkylene glycol or a polyether alcohol. Polyethylene terephthalate is an example of a suitable polyester resin. Chopped up, used polyester containers are a source of such filler particles.

Suitable plastics also include synthetic fibers -- e.g., reclaimed fibers from discarded carpet, e.g., nylon, polyolefin, or polyester carpet fibers.

Suitable polyurethanes include, for example, polyether polyurethanes and polyester polyurethanes.

Among the various plastic fillers that can be used in the core material are expandable polymer beads. By "beads" we here mean particles of any geometry, e.g., spherical, cylindrical, or lumpy. Expandable polymer beads are cellular pellets of expandable polymer that often are used to form lightweight molded objects. Created in a more or less granular form, and with an expanding agent in the cells, typically the beads are pre-foamed, or "pre-expanded," by heating to a temperature above their softening point, which often will be in the range of about 165 - 185° F., until they foam to give a loose aggregate of the desired bulk density. The pre-foamed particles, which retain their cellular structure, may then be placed in a mold or other cavity and heated with live steam, causing them to sinter and fuse together to form a lightweight, cellular solid whose dimensions correspond to those of the mold cavity. When fully expanded, the beads often will have a diameter that is about 2 to 4 times that of the unexpanded, or "raw," beads.

-8-

Depending upon the manner in which the rigid core material is made, the beads can possibly be heated to such a high temperature that they will sinter while enclosed in the resinous matrix of the core material. If so, at least a substantial portion of the beads will then lose their cellular structure, creating gas-filled pockets, of various sizes, in the foam, which are lined with the polymer of which the cellular structure was formed. It appears that isolated spherical beads generate relatively spherical pockets. These hard, polymeric globules can lower the density of the core material without significantly lowering its crush resistance. Indeed, it appears that they may even enhance the crush resistance.

5

The source of the heat necessary to cause bead sintering can be an exothermic reaction that generates the matrix resin in which the beads are trapped. Thus, for example, the matrix resin can be formed by blending the necessary reactants to generate an exotherm having a peak temperature in the range of about 185-285°F.

10

Chief among expandable polymer beads are expandable polystyrene (EPS) beads and expandable polyolefin (EPO) beads.

15

Methods of making expandable polystyrene beads are well known. As disclosed in U.S. Patent Nos. 3,991,020; 4,287,258; 4,369,227; 5,110,835; 5,115,066; and 5,985,943, for example, all of which are incorporated herein by reference, EPS beads may be made by polymerizing styrene in an aqueous suspension, in the presence of one or more expanding agents that are fed at the beginning, during, or at the end of polymerization. Alternatively, they may be made by adding an expanding agent to an aqueous suspension of finely subdivided particles of polystyrene.

20

The expanding agent, also called a "blowing agent," is a gas or liquid that does not dissolve the styrene polymer and which boils below the softening point of the polymer. Examples of suitable blowing agents include lower alkanes and halogenated lower alkanes, e.g., propane, butane, pentane, cyclopentane, hexane, cyclohexane, dichlorodifluoromethane, and trifluorochloromethane. Often the

25

-9-

beads contain about 3 to 15%, based on the weight of the polymer, of the blowing agent. Preferably, the blowing agent will be present at a level of about 3 to 7%.

By "polystyrene" is here meant a styrene homopolymer or copolymer containing 50 wt.% or more, preferably at least 80 wt.%, of styrene. Examples of suitable comonomers are α -methylstyrene, ring-halogenated styrenes, ring-alkylated styrenes, acrylonitrile, esters of acrylic or methacrylic acid with alcohols having from 1 to 8 carbon atoms, N-vinylcarbazole, and maleic acid or anhydride. A minor amount of a copolymerized chain-branching agent may be included in the polymer as well. Suitable such agents are compounds containing at least two α , β -ethylenically unsaturated groups, such as divinyl benzene, butadiene, and butanediol diacrylate. Branching agents are generally used in an amount of about 0.005 to 0.05 mol %, based on the styrene.

The polystyrene in the EPS beads usually has a weight average molecular weight in the range of about 130,000 to about 300,000.

EPS beads come in different unexpanded particle sizes. Generally, a bead's longest dimension (e.g., its diameter), on a weight average basis, will be in the range of about 0.1 to 6mm, often about 0.4 to 3mm. It is thought that unexpanded particle sizes in the range of about 0.4 to 1.6mm are preferred for the beads used in the present invention.

Unexpanded polymer beads vary as to their expansion capability, i.e., how large they can get when heated to expansion temperature. In part, this is a function of how much blowing agent they contain. The expansion capability of a polymer bead can be reported in terms of the bulk density of the loose aggregate the beads will form when they are fully expanded ("fully expanded density"). By "fully expanded" is here meant the expansion that results from the "two pass" expansion process described in Example 2 of U.S. Patent No. 5,115,066. This entails the use of a Tri Manufacturing Model 502 expander (or equivalent), operated at an inlet steam temperature of about 211° F. and an inlet steam flow rate of approximately 74 pounds per hour. The first-pass throughput rate is about 208 pounds per hour.

-10-

A fluidized bed drier, blowing ambient air, is used to cool the resulting prepuff. After aging for 3 hours at ambient temperature and humidity, the prepuff is run through the expander again, under the same conditions, except operating at a throughput rate of about 217 pounds per hour.

5 It is thought that the use of EPS beads having a capability of reaching a fully expanded density in the range of about 0.5 to 4.5 pounds per cubic foot (pcf), e.g., about 1 to 3 pcf, is preferred in the present invention. Examples of some commercial EPS beads that can be used in the present invention are Types 3371, 5371, and 7371 from Huntsman Chemical and Types BFL 322, BFL 422, BF 322, 10 BF 422, and P 240 from BASF Corporation.

15 As examples of expandable polyolefin beads may be mentioned expandable polyethylene (EPE), expandable polypropylene (EPP), expandable polybutylene (EPB), and copolymers of ethylene, propylene, butylene, 1,3-butadiene, and other olefin monomers, particularly alpha-olefin monomers having from 5 to 18 carbon atoms, and/or cycloalkylene monomers such as cyclohexane, cyclopentene, cyclohexadiene, and norbornene. Propylene/ethylene copolymers and propylene/butylene copolymers may be preferred.

20 Methods of making expandable polyolefin beads are disclosed, for example, in U.S. Patent Nos. 6,020,388; 5,496,864; 5,468,781; 5,459,169; 5,071,883; 4,769,393; and 4,675,939, all of which are incorporated herein by reference.

25 Expandable polymer beads may contain other additives to impart specific properties either to the beads or to the expanded products. These include, for example, flameproofing agents, fireproofing agents, nucleating agents, decomposable organic dyes, lubricants, fillers, and anti-agglomerating additives. As disclosed in U.S. Patent No. 6,271,272, incorporated herein by reference, the beads may also include additives, e.g., certain petroleum waxes, that quicken the rate of expansion when the beads are heated to expansion temperature. Depending

-11-

on the intended effect, the additives may be homogeneously dispersed in the beads or present as a surface coating.

If expandable polymer beads are used as filler solids in making the core material for the present invention, they can be mixed with the matrix resin precursor mixture in either the unexpanded, partially expanded, or substantially fully expanded state. Preferably, however, by the time the matrix resin has set, the polymer beads will have undergone at least a partial expansion, as well as a sintering, to yield the polymeric globules entrapped in the matrix. This is described in greater detail in a copending U.S. patent application, entitled "Improved Process of Making Rigid Polyurethane Foam," filed March 22, 2002, by Arthur J. Roth, one of the present inventors. The specification of that application is incorporated herein by reference.

Rubber Fillers

Pieces of natural or synthetic rubber can be used as a filler solid also, e.g., rubber made of styrene-butadiene resin, polybutadiene, or polyisoprene. A preferred source of rubber is used and scrap tires, which can be pneumatic tires or non-pneumatic tires.

Older tires are preferred because they generally have fewer volatives and are less elastomeric. Truck tires are preferred over passenger tires, because they have greater rigidity. Preferably any metal in the tires from metal belts amounts to no more than about 3 weight percent of the rubber, most preferably one percent or less, especially if the composite structure material is to be used to construct shipping pallets. There are a number of reasons. The more metal content, the greater the pallet weight, which increases shipping costs. Also, the presence of pieces of metal can cause additional wear and tear on the equipment used to make the composite structural material, e.g., augers, extruders, and injection heads. Also, if allowed to remain in or among the tire fragments used as filler solids, metal cords, shards, or splinters can project through the laminar covering when the

-12-

composite is under compression and damage the load on the pallet or present a safety hazard to material-handling personnel.

Ground up used tire rubber is available commercially and comes in different particle sizes. Perhaps preferred for the present invention is No. 4 tire granule (minus 10 mesh), preferably with the tire cord (referred to as "fluff") not removed. Both black and white tire crumb can be used.

When used, granulated tire rubber might constitute, for example, about 20 to 90 percent of the volume of the finished material's core.

Scrap tire rubber is a relatively inexpensive filler, on a volume basis. It is rather heavy, however, and if it is important that the specific gravity of the composite structural material be at or below a certain value, the amount of tire rubber that can be used may be limited accordingly. Thus, for example, if the composite structural material is to be used as synthetic boards to fabricate shipping pallets, specific gravity (i.e., finished pallet weight) is a concern. It is preferred that the core material of such boards have a specific gravity of about 0.65 g/cc or less, e.g., a finished density of about 40pcf or less. Generally that means using a core material that contains 45 weight percent or less of rubber.

If, on the other hand, the structural material is to be used for an application that is less demanding in terms of specific gravity, e.g., as for range fencing, stationary decking, or highway guard rail posts or blocks, such composites can have specific gravities as high as, say 0.95, or even 1.10, g/cc, e.g., a finished density of up to as high as 60 or 70 pcf. This often permits the use of rubber concentrations of up to 70 or 85 percent, based on the weight of the core material.

The filler particles can be in any shape, e.g., fibrous, flake; or granular (including spherical, e.g., silicate spherules and hollow polymeric spherules, including polymeric microspheres).

As regards the size of the pieces of filler used in the core material, preferably their longest dimension will be no more than about 50% of the thickness of the composite structural material. Thus, for example, if the composite structural

-13-

material is a board having a thickness of one inch, substantially all of the pieces of filler solid preferably will have a longest dimension that is no more than about $\frac{1}{2}$ inch.

5 Preferably the nature of the matrix resin, the nature and amount of the filler particles (if any), and the degree of foaming (if any) of the matrix resin will all be chosen so that the core material has a crush resistance of about 300 pounds per square inch (psi) or more, e.g., in the range of about 300 to 2500 psi. (This refers to the amount of pressure required to reduce the core material's thickness by ten percent.) If the matrix resin is foamed, such crush resistance can be measured, for example, by ASTM D 1621-94, entitled "Compressive Properties of Rigid Cellular Plastics."

10

15 The crush resistance of a rigid solid is generally directly related to its density, and so is also related to the ability of the material to hold a nail. (The denser the rigid solid, the more able it generally is to hold a nail.) The present invention is particularly useful for providing wooden-board-substitutes for shipping pallets. For the deck boards of shipping pallets, which do not have to hold nails, and for which the lowest feasible specific gravity is often desired (to lighten the load), a crush resistance as low as about 300 psi (with its concomitant low density) can generally be used, although a crush resistance of at least about 20 1100 psi is preferred. For stringers in shipping pallets, which generally do have to hold nails, generally the crush resistance should be at least about 1800 psi, and most preferably at least about 2200 psi.

20 For many applications it will be preferred that the composition and amounts of the matrix resin and filler particles (if any) be such that the structural material has a coefficient of linear thermal expansion that is in the range of about 2.5 to 3.5 $\times 10^{-5}/^{\circ}\text{F}$.

THE WEB MATERIAL

The web material in the laminar covering is rigidified paper or cloth. Because it is less expensive than cloth, paper is preferred. When paper is used,

-14-

preferably it will have a thickness in the range of about 0.015 to 0.020 inch. Most preferred is a thickness of about 0.017 inch. The paper can be a web of various fibers, e.g., one or more types selected from the group consisting of cellulosic, glass, carbon, metal, and synthetic resin. Examples of suitable synthetic resin fibers include polyamide fibers and polyester fibers. Most preferably the fibers are oriented in the paper, e.g., as in paper in which the fibers are oriented in the machine or warp direction, also sometimes called the "milled direction."

5

10

15

20

For reasons of economy it is believed to be preferable to use a paper that is made at least primarily of cellulosic fibers, e.g., from wood pulp. A preferred cellulosic paper is kraft linerboard paper, for example having a basis weight (or "grade code") of at least about 65 lbs. per msf (thousand square feet), e.g., about 65 to 100 lbs. The preferred moisture content is about 7 to 9 wt. %, e.g., approximately 8%. The Mullen value preferably is about 130 or 140 to about 145 psi. The paper's CD Ring Crush value is preferably about 120 or 130 to about 140 lbs.

One suitable paper is 100% recycled standard linerboard paper having a basis weight of about 69 lbs. Such is manufactured, for example, by Gaylord Container Corporation. Another suitable paper is 25% recycled kraft linerboard having a basis weight of about 90 lbs. Such can be obtained, for example, from Longview Fibre Company, of Longview, Washington, under Specification No. 5204. Virgin paper also can be used, of course, but it tends to have lower capillarity than recycled paper, which, for that reason, is generally preferred.

Generally it is preferred that the paper contain at least about 40 wt.% of recycled material.

25

As will be explained later herein in more detail, it is preferred that a resin be used to bond the cords to the web material and to impregnate and stiffen the web material. In such an embodiment it can be useful if the outermost ply of web material (e.g., paper) includes a barrier layer to prevent the resin from bleeding through the web material. The barrier layer may be comprised, for example, of a

-15-

resin, e.g., poly(vinyl alcohol), which can be an effective barrier to the migration of an epoxy resin through the thickness of the web material. By use of this feature, if the outermost ply of web material has a core-facing layer that is resin-permeable and a layer external to that that bars resin migration, the resin, while stiffening the web material, will not bleed to the outer surface of the composite, where it could possibly foul the contact surfaces of a molding apparatus that is used to hold the assembly of core, web material, and cording in the desired shape while the resin sets.

5

If desired, after the composite is removed from the mold, the resin-free outer layer of the bifurcated paper can be coated (e.g., sprayed) with a finishing composition, to impart desired physical and/or chemical properties to the outer surface of the composite. An example of such a multi-layered paper is Specification No. 6228 from Longview Fibre Company.

10

Another option is to concentrate a fireproofing agent in the outer layer of a barrier-layer-containing paper, where the agent will be most effective. This is best done if the paper comprises two external porous layers (one of each side) and a barrier layer sandwiched between the two.

15

THE PARALLEL CORDS

20

If the composite is elongated, it will often be preferred that the cording used in the laminar covering be aligned in the long direction. Alternatively, the cording can run perpendicularly or diagonally to the composite's long direction. For example, if the elongated composite has a round cross section, the cording can be wound spirally around the core, preferably surrounding the core with a uniform layer of cording. When a spiral-wound composite is intended to be used as, for instance, a post to support a highway guard rail, a suitable covering may consist of two plies of paper with one ply of polyester cording, in the form of a scrim, sandwiched between the two plies of paper.

25

Preferably the cording used in the laminar covering has a tensile strength in the range of about 5 to 18 pounds per cord, most preferably about 16 pounds. The

-16-

cording preferably has a breaking tenacity of about 0.67 to 1.10 gf/TEX, most preferably about 0.85 gf/TEX.

The cording can be made of continuous filament or staple fibers.

Monofilament cording can be used, but cording made of a plurality of continuous filaments (so-called "multifilament" cording) is preferred. Preferred multifilament cording is that which is made of about 40 to 70 filaments. If multifilament cording is used, the filaments can be twisted or untwisted. If twisted, it is preferred that the cord have not more than 3.25 twists per inch.

As for breaking elongation, preferably the cording's is in the range of about 10 to 50%, e.g., about 20 or 25% to about 45 or 50%. Most preferred for monofilament cording is a breaking elongation of about 30 to 40%, e.g., about 35%. Most preferred for multifilament cording is a breaking elongation of about 15 to 20%, e.g., about 17%.

The cording can be made in whole or in part of either natural or synthetic fibers or filaments, including fibers/filaments of synthetic resin, glass, carbon, or metal. Synthetic resin fibers/filaments are often preferred, e.g., polyester, polyamide (such as nylon and poly-paraphenylene terephthalamide), or polyolefin fibers or filaments. Glass fibers/filaments generally provide greater stiffness in the composite structural material. For certain uses, e.g., fence boards, a better ability to bend might be preferred; in that situation polyester fiber/filaments generally work better than fiberglass.

If the cording is made of shrinkable fibers/filament, preferably it is heat stabilized prior to being used to construct the composite structural material of the present invention.

When made of a monofilament, the cording preferably has a diameter of about 8 to 15 mil (i.e., about 0.008 to 0.015 inch), most preferably about 10 to 12 mil.) When made of multifilament, the cording preferably has a denier of about 600 to 1,000, most preferably about 900.

-17-

As for the density of the parallel cords in the band -- i.e., the number of cords per inch of width of the band -- the preferred level varies in inverse relationship to the diameter or denier of the cording. The thicker the cording, the lower the preferred density. Generally, however, the density will preferably be at least about 10 or 12 cords per inch of band width ("lateral inch"), and usually not more than about 35 cords per lateral inch.

The parallel reinforcing cords can be unconnected one to the other, or they can be laterally connected, e.g., by cross-cording. The latter arrangement has the advantage that it can help keep the longitudinal cords in place during the formation of the laminar covering. An advantageous way of providing the cords in this fashion is to use a strip of cloth in which the longitudinal cords constitute the warp, i.e., the "yarn," "fiber," or "thread" that is in the cloth's "machine direction." By "cloth" is here meant either a woven cloth or a cross-laid scrim. The latter is a nonwoven netting formed by laying parallel rows of continuous yarn or thread in the warp direction and then laying parallel rows of cross yarns or threads on top of that layer, at a 90 degree angle thereto, and bonding the two layers together at the cord intersections, e.g., either by thermal bonding or by use of a glue. When cross-laid scrim is used, the warp side can either face outwardly from the composite or inwardly. Preferably, however, it will face outwardly and will be next to a layer of web material.

Generally it is preferred that any cloth that is used have a warp direction tensile strength that is within the range of approximately 90 to 200 pounds per lateral inch (pli), most preferably approximately 155-185 pounds per lateral inch. By this is meant the amount of longitudinal stress necessary to tear apart a one-inch-wide band of the cloth, running in the warp direction.

If the cloth comprises any shrinkable fibers/filament, preferably those will be heat stabilized before the cloth is used to construct the composite of the present invention.

-18-

It is preferred that the cross-cording (i.e., the woof or weft of the cloth, also sometimes called the "pic" or the "fill") be of a smaller diameter and/or of a lesser density (fewer cords per inch of cloth) than the warp. Thus, for example, the diameter or denier of the warp cords may be about 1.8 to 2.5 times that of the woof cords, and the density of the warp cords (i.e., the number of cords per lateral inch of the cloth) may be about 1.5 to 3 times the density of the woof cords (i.e., the number of cords per longitudinal inch of the cloth.)

When woven cloth made of 10-12 mil monofilament in the warp direction is used, preferably the warp density will be at least about 20 cords per lateral inch of the cloth, e.g., in the range of about 20 to 35 cords per lateral inch of the cloth. The woof cords of such a cloth preferably will have a diameter in the range of about 4-8 mil, most preferably about 6-8 mil. The woof density for such a cloth may be, for example, about 10 to 18 cords per longitudinal inch of cloth.

Among the woven cloths that can be used very effectively to supply the reinforcing cords are those composed of about 8-12 mil polyester monofilament as the warp and about 6-8 mil polyester monofilament as the woof. Advantageously such polyester cloth has approximately 20-30 cords/inch in the warp and approximately 10-15 cords/inch in the woof. Prototype fabric No. XF368080 from Industrial Fabrics Corporation, of Minneapolis, Minnesota, is a woven polyester cloth that meets these specifications. Its warp cording has a diameter of approximately 10 mil, a tensile strength of approximately 5.2 pounds per cord, and a breaking elongation of approximately 46%. The density of the warp is approximately 27-29 cords per lateral inch. The woof cording has a diameter of about 8 mil. It is estimated that a one-inch-wide strip of this cloth has a tensile strength in the warp direction of approximately 95-105 pounds and an elongation at break of approximately 46%.

Also suitable is the same woven polyester cloth as just described, but having a warp cord density of only 24 cords per lateral inch. It also can be obtained from Industrial Fabrics Corporation. That fabric has a warp direction

-19-

tensile strength of approximately 91 pounds per lateral inch and an elongation at break of approximately 46%.

An example of a suitable cross-laid scrim is Connect™ scrim from Conwed Plastics, Inc., of Minneapolis, Minnesota. One embodiment thereof has a warp composed of untwisted polyester multifilament cord (60 filaments per cord) having a denier of about 1000. The warp has a cord density of 12 cords per lateral inch. The warp cording has a tensile strength of about 17.5 pounds per strand of the cord. A one-inch-wide, warp direction strip of the scrim has a tensile strength of about 185 lbs., a breaking elongation of about 24%, and a breaking tenacity of about 0.92 gf/TEX.

Preferably the laminar covering will comprise a band of parallel cords (which, as indicated, can be a strip of cloth) that covers at least one side of the structural material. For example, at least about 25% of the cross-sectional circumference of the material can be covered with one or more bands of parallel cords. If the material is rectangular in cross section, it is most preferred that at least two opposite sides be covered with bands of the cords. Most preferably, all sides of the structural material will be covered with bands of the cords. If the cross section is an elongated rectangle and the material is to be used as deck boards for shipping pallets, e.g., as a substitute for 1" x 4" or 1" x 6" lumber, it is preferred that at least the two wide sides of the board be covered with bands of the cords.

For other uses, however, if only two sides are covered with the bands of cords, it might be preferred that they be the narrower sides. Thus, for example, in shipping pallets the stringers often are wooden 2 x 4s or 3 x 4s set "on edge." If the structural material of the present invention is to be used in place of such wooden boards, then it is preferred that at least the two narrow sides be covered with bands of the cords.

Most preferred for shipping pallets, however, is that all four sides of both the deck boards and the stringers be reinforced with bands of parallel cords. In this way not only is the pallet able to withstand large loads, it also is more resistant to

-20-

damage along the vertical surfaces of the boards, e.g., due to being hit by fork lift tines.

Where all sides of a board-shaped composite are to be covered with bands of cords, the four bands need not always be constructed the same. Thus, for example, one pair of opposite sides might require bands of lower tensile strength than the other two sides.

If the cording is being supplied by a scrim and it is desired to use different cord bands (e.g., having different tensile strengths) on different sides, one can use a multi-zone scrim that is wide enough to wrap around the core of the board. If it is a four-zone scrim, each zone will be the width of (and will register with) one of the four sides of the board. Different warp cords and/or different cord densities can be used in the four different zones, while the cords and cord densities in the woof direction are kept uniform.

As far as dimensions are concerned, the present invention is very useful for the construction of board-shaped composites having a thickness of about $\frac{1}{2}$ inch to 8 inches and a width of about 2 to 48 inches and pole-shaped composites having a diameter in the range of about 2 to 18 inches, although it certainly is not limited to such materials.

For maximum strength, it is preferred that at least some of the reinforcing cords in the laminar covering be bonded to the web material in a pretensioned state. The amount of tension can be expressed in terms of how much the cord is stretched. Thus, every cord has an elongation-at-break value that is expressed as how much, in percent, the cord's length can be increased by stretching, before the cord breaks. The more it is stretched, the greater the tension on the cord. In the present invention it is contemplated that it generally will be preferred that the cord not be stretched (i.e., elongated) beyond about 85% of its capacity. Thus, if its elongation at break is 30%, say, then it is preferred that the cord not be lengthened by tension to more than 125.5% of its starting length.

-21-

As for the minimum amount of stretching, it is preferred that the cord be stretched to at least about 10% of its capacity, most preferably at least about 20%, 30%, or 40% of its capacity. Often the most preferred range will be about 50 or 60% to about 80% of its capacity. Generally it will be preferred, when cloth is used as the source of the parallel cords, that it be pretensioned in the warp direction to a value of at least about 10 pli, most preferably at least about 50 pli, e.g., at least about 75 or 100 pli.

5

DISSIMILAR EMBEDMENTS

10

The laminar covering can optionally contain an embedment of a material that is dissimilar from the core and covering, and which has a physical property that can be measured from a distance, e.g., a property such as inductance, reflectance, thickness, density, or two-dimensional shape, which can serve as an identifying feature of the composite, or the article in which the composite is included. The material can be composed, for example, of a metal, a sulfate, a chloride, or graphite. Examples of suitable metals include aluminum, copper, gold, nickel, cadmium, zinc, bronze, chromium, cobalt, potassium, chrome, lead, tin, and silver. A metallic layer deposited on a substrate can be used, for example.

15

20

The embedment can be coterminous with the cording and/or web material, or it can be a smaller section. The embedment's physical property can be detectable by, for example, diffraction or refraction techniques using external-source electromagnetic radiation, e.g., x-rays or radio waves. The embedment can even include a circuit pattern that emits a signal when contacted by an electromagnetic field.

25

By use of this embedment feature, the composite (or an object made therefrom, such as a shipping pallet) can be provided with a type of tagging device, e.g., to indicate the nature of one or more components of which the composite or object is made, or where and/or when it was manufactured, or by whom it is owned.

-22-

OTHER LAYERS OR COMPONENTS

The laminar covering may optionally comprise one or more plant-growth repellants. Thus, for example, the outermost coating on a composite that is to be used as a highway guardrail post can contain a chemical that repels climbing plants such as ivy.

Another chemical additive that can optionally be included in the laminar covering is a fire or flame retardant. Similarly, reflective particles can be embedded in the outermost coating, e.g., reflective particles of the type used in highway safety markers. Pigments and/or dyes can be included as well, for decoration or identification purposes. Also, an anti-corrosion chemical can be included, as, for example, when it is anticipated that the composite might come into contact with a chemical that could otherwise react with, and degrade, the laminar covering. Thus, for example, a board-like composite that is to be used to construct pallets for the shipping of drums containing a particular corrosive chemical can contain in its outermost coating a component that confers resistance to that chemical, in case of leakage.

For some purposes it may be important that the outermost surface on one or more sides of a composite have a coefficient of friction that is within certain defined limits. Thus, for example, the top surface of deck boards on a shipping pallet should have a high enough coefficient of friction that load shifting will not be a problem during transit, but not so high a coefficient that it is unacceptably difficult to slide freight on or off the pallet. To help set the desired co-efficient of friction, the outermost coating on the laminar covering can have friction-increasing asperities projecting from the surface. Such asperities can be provided by use of the same techniques as are used to make pickup-truck bedliner surfaces slip resistant, e.g., by embedding a grit material such as sand in the coating, by forming the polymeric coating in such a way that it is non-smooth, or by stippling the surface with droplets of a resin that leaves small bumps on the surface.

-23-

For decoration or other purposes, the outermost layer of the laminar covering can optionally be a wood veneer, e.g., having a thickness of at least about 4 mil. If the thickness is about 20 mil or more, such a veneer generally functions as a structural membrane -- i.e., it adds strength to the composite.

5

THE BONDING/STIFFENING RESIN

10

The cords preferably are bonded to the web material by a resin, most preferably a resin selected from the group consisting of epoxy, polyurethane, acrylic, nitrile, butyl, allyl, urea-melamine, vinyl ester, phenolic, silicone, and cyanoacrylate resins. A thermosetting resin, e.g., a thermosetting vinyl ester resin or a thermosetting epoxy resin, is most preferred. If the core material comprises a matrix resin, then the bonding resin preferably is compatible with the matrix resin, i.e., will adhere thereto. In this regard, certain polyurethane and epoxy resins are known to be compatible, as are certain phenolic and vinyl ester resins.

15

To make the laminar covering dimensionally stable, it is preferred that the web material be impregnated with a set resin, most preferably a cured thermosetting resin. Again, compatibility with any bonding resin and matrix resin that is used is desired. Preferably the same binding resin that is used to bond the cords to the web material is also used to impregnate and stiffen the web material.

20

Epoxy resins are perhaps preferred for the stiffening resin and the bonding resin. Both one-component epoxy resin systems that require elevated temperatures to cure and two-component epoxy resin systems that can cure at room temperature can be used. The two-component systems have separate resin and hardener components.

25

As for viscosity, the systems can be thin enough to be sprayable or so viscous that they have to be applied with, for example, a bath roller or a "pin" roller. An example of the sprayable type is Product Code R 88-14B/H 88-14E from Copps Industries, Inc., of Mequon, Wisconsin, which is a two-component system having a viscosity (immediately after mixing) of about 1,480 cP, when mixed at a weight ratio of 4.2 parts resin to one part hardener. Its gel time at 77°F.

-24-

is approximately 24 minutes, as measured by ASTM Test D2471. An example of a system that also can be used, but which is too viscous to be sprayed effectively, is Copps Industries R 88-14A/H -14D, which is a two-component system having a viscosity of about 3,000 cP, when mixed at a weight ratio of 3.1 parts resin to one part hardener, and a gel time at 77°F of about 42 minutes.

5

System R 88-14B/H 88-14E is designed to bind laminated structures and will bind well to cellulosic paper, fiberglass mesh, polyurethane foam, and recycled rubber, among other materials. R 88-14A/H 88-14D also is designed to bond to a wide variety of similar and dissimilar materials. Also suitable is a developmental epoxy resin system from Copps that is designated R 900/H 900.

10

The laminar covering can be comprised of a single layer of web material and a single layer of cording. Alternatively, a plurality of layers of one or both can be used. Where a plurality of parallel-cords layers are used, preferably a web layer will be interleaved between every two parallel-cords layers. Preferably, the covering will comprise at least one combination of a layer of parallel cords bonded to a web layer that is exterior to the parallel-cords layer. Thus, for example, excellent strength can be obtained by a four-ply arrangement, starting from the core, of cord layer/web layer/cord layer/web layer.

15

The properties of the composite will vary depending upon its aspect ratios, i.e., the ratio in a particular cross-sectional direction of the thickness of the composite's laminar covering (or facia), T_f , to the composite's total thickness, T . Thus, for example, a composite in the shape of a 1" x 4" board that is surrounded with a 1/8" thick facia will have a thickness aspect of 0.25 ($T_f = 2 \times 1/8" = 1/4"$; $T = 1"$) and a width aspect of 0.062 ($T_f = 2 \times 1/8" = 1/4"$; $T = 4"$). Generally it is preferred that, in at least one cross-sectional direction, the composite have an aspect of at least 0.1.

20

Facia of different thicknesses can be used on different sides of the composite, even on opposite sides. Thus, for example, where the composite is a board that will be subjected to minimal lateral loads but extensive vertical loads,

-25-

one might save expense by using thinner facia on the sides than on the top and bottom. In a situation in which the board will be subjected to strenuous vibrations, it may be desirable to use a thicker wall on the top than on the bottom.

5 Greater surface smoothness generally can be obtained if the outermost of all the parallel-cords and web layers is a web layer. This can be advantageous in a case in which the structural material has to be kept sanitary. If, for example, the structural material is to be used as a board in a shipping pallet (e.g., as either a stringer or a deck board), it might have to be sterilized when the pallet is used in areas of food preparation or handling. This can entail steam treatment and/or washing with disinfectants containing bactericides, such as chlorine-containing reagents. The composite structural material of the present invention, especially when having a resin-stiffened web material at its outer surface, can be easier to sanitize than boards of real wood, due to its having fewer cracks, crevices, and pores in which microorganisms can reside, and possibly escape the heat or contact
10 with the disinfectant.
15

MAKING THE COMPOSITE STRUCTURAL MATERIAL WITH A SEGMENTED COVERING

20 The laminar covering can be in one piece or in longitudinal sections. For ease of manufacture, it might be preferred that the laminar covering be comprised of two mating C channels that run the entire length of the structural material. The C channels would be opposed, their openings facing each other. It is preferred that the two channels overlap along their longitudinal edges and that they be conjoined, for example with the same thermosetting resin as is used to rigidify the web material. If the cross-sectional shape of the structural material is a non-square rectangle, then it is preferred that each of the C channels covers one of the wide sides of the structural material -- i.e., that the overlapping edges of the two C channels be located on the narrow sides.
25

The C channel version of the composite structural material of the present invention can be made, for example, by a method comprising the following steps:

-26-

- a) obtaining a first elongated C channel of a porous web material that is impregnated with a thermosetting resin precursor mixture and orienting the channel with the C facing up;
- 5 b) impregnating a strip of cloth with a thermosetting resin precursor mixture that is compatible with the resin precursor mixture in the web material;
- c) laying said strip of cloth on the inside bottom of the first C channel, with the warp running in the lengthwise direction of the channel, so as to extend the length of the channel;
- 10 d) optionally placing one or more additional layers of said web material and/or cloth on the C channel;
- e) depositing on the top layer in said C channel a fluid mixture of a matrix resin precursor composition and pieces of a filler solid, the matrix resin precursor composition being compatible with both the resin precursor mixture in the web material and the resin precursor mixture in the cloth;
- 15 f) covering the first C channel with a second C channel of a porous web material that is impregnated with a thermosetting resin precursor mixture that is oriented with the C facing down, so that the vertical sides of the two channels overlap and touch each other and the two C channels define a core space between them; and
- 20 g) holding the two C channels together under conditions that are conducive to the setting of (i) the matrix resin in the core space, (ii) the thermosetting resin in the porous web material, and (iii) the thermosetting resin in the cloth, and for a length of time sufficient for all three resins to set, whereby the two C channels become bonded together where they overlap, the cloth strip becomes bonded to the first C channel, the core space becomes filled with the mixture of matrix resin and pieces of filler solid, and the matrix resin becomes bonded to the cloth and the web material.

The foregoing steps do not have to be performed in the order listed. For example, the strip of cloth can be laid on the porous web material either before or

-27-

after the latter is forced into a C-channel shape. Also, the impregnation of the web material and the cloth with thermosetting resin can occur before or after the layering of the cloth on the web material.

To keep the density and cost of the structural material relatively low, it is preferred to use a matrix resin that is foamable, and to deposit the mixture of matrix resin precursor composition and filler solid (if used) on the topmost layer in the bottom C channel in a volume amount that is insufficient, without foaming, to fill the cavity between the two C channels of web material. In such a method, the two C channels are held together under conditions that are conducive to the forming, foaming, and setting of the matrix resin, whereby the mixture of resin and filler solid (if used) expands to fill the cavity between the two C channels. The foaming can be caused by the release, expansion, or generation of one or more gases in the resin precursor mixture, e.g., a gas selected from the group consisting of carbon dioxide, nitrogen, hydrofluorocarbons (e.g., HFC 245SA and HFC 134A), chlorofluorocarbons, and lower alkanes, e.g., pentanes. Resin systems for generating foamed thermoset resins are well known in the art, and include, for example, the aforementioned polyurethane resin systems.

For maximum composite strength, when using the C channel method of fabrication, the second (top) C channel that is used in step e is underlaid with a second strip of cloth that also is impregnated with a thermosetting resin precursor mixture that is compatible with the resin precursor mixture in the web material. That cloth also should extend the length of the second C channel, and it too should become bonded to both the second C channel and the matrix resin, during step f.

Preferably, in both C channels the layer that contacts the matrix resin precursor composition is a layer of porous web material, most preferably paper. E.g., in each C channel three layers in all may be used: two layers of porous web material, with a layer of cloth sandwiched between them. (In such a construction, it is preferred that the innermost web material have no resin-barrier layer.) Using web material, rather than cloth, as the innermost layer appears to provide for more

-28-

even pressure distribution during the setting of the core's matrix resin and, therefore, a more uniform composition of the ensheathed core material.

The C channel method of fabrication can be run on a substantially continuous basis by pulling each of the porous web material strips and the woven cloth strip or strips off its own supply roll. For each C channel, the porous web material can be pulled through a wetting station where it is impregnated with the thermosetting resin precursor mixture. Depending on the viscosity of the thermosetting resin precursor mixture, wetting might be accomplished by spraying, gravure printing a pattern of the mixture on the web material, or passing the web material through a bath of the mixture. Either before or after the wetting station, each run of the web material can also be pulled through a forming station where it is folded into the desired C channel cross section.

Meanwhile, each strip of cloth can be pulled through a wetting station where it is impregnated with its thermosetting precursor mixture. One of the impregnated strips of cloth is then made to lie on the inside bottom of the first (upward facing) C channel, following which the fluid mixture of the matrix resin precursor composition and pieces of filler solid is deposited on top of the cloth. The second impregnated strip of cloth is made to lie against the underside of the second (downward facing) C channel, which is poised above the first C channel.

After the station at which the fluid mixture is deposited onto the upward facing first C channel, that channel can be covered with the cloth-lined, downward-facing, second C channel. If the dimensions of the two C channels are the same, the top one can be slightly offset, in the lateral direction, so that one of its side walls (i.e., its vertical walls) rides outside one of the side walls of the bottom C channel, while the other side wall of the top C channel rides inside the other side wall of the bottom C channel. Alternatively, one of the C channels can be made slightly wider than the other, so that it completely straddles (i.e., overarches) the other C channel.

-29-

Once they are mated in this manner, the two runs of resin-impregnated cloth and two runs of resin-impregnated web material can be simultaneously pulled through a continuous molder that is maintained at the proper temperature to cause the matrix resin, the thermosetting resin in the porous web material, and the thermosetting resin in the cloth all to form and set. It might be preferred, however, before entering the continuous molder, that the resin-precursor-mixture-impregnated web material and cloth be heated. This can flash off some solvent in the mixture(s) and/or accelerate the reactions that have to occur and, as a consequence, shorten the time that the mated C channels have to remain in the continuous molder.

10

15

20

25

The continuous molder can be, for example, at least one tractor mold, which sometimes is referred to as a type of "endless flexible belt mold." This is a type of mold in which cooperating half-mold segments revolve on opposed ovoid conveyor tracks to grip between them a section of an axially moving, continuous linear feed material and hold it for a time, while the material and the abutting half-mold segments continue to travel forward. The half-mold segments are connected, back and front, to identical segments, much like links in a tractor tread. Each pair cooperates to form an external die that holds its section of the feed material in the desired shape as the material solidifies. The half-mold segments can be equipped with temperature-control means to cause the synthetic resin in the feed material to become set by the time the segments reach the end of their forward run. There the opposed segments separate, releasing the section of the feed material, and each segment circles back to the beginning to grip another section of the feed material. Meanwhile, the intervening length of feed material has been gripped and treated by other pairs of half-mold segments. One example of a moving mold of this type is disclosed in U.S. Patent No. 5,700,495 to Kemerer, et al., which is incorporated herein by reference. The forward run of the tractor mold preferably is long enough that, by the time the two C channels emerge from the mold, the impregnating resins and the matrix resin have all been formed and are set. If necessary,

-30-

however, the feed material can be passed through a series of two or more tractor molds in order to hold the material in the desired shape until the resins in it are all set.

The mixture of matrix resin precursor composition and filler solid can be preformed and pumped as one uniform mixture through an applicator conduit, so as to land on the topmost layer in the bottom C channel. Alternatively, the components of the mixture can be kept separate in two or more segregated streams, and those streams can be blended in a mixing nozzle, or even in the air space between the exit openings of their respective applicator conduits and the surface of the layer upon which the components land. In this way, it can be arranged that none of the material streams is independently settable; instead it requires that two or more streams be blended before a settable mixture is obtained. Thus, the method can be performed much like reaction injection molding (called RIM molding) in which a necessary curing catalyst and/or cross-linking agent is delivered to the fill hole of a mold cavity in one stream, while a monomer or prepolymer that needs to be mixed with the catalyst and/or cross-linking agent in order to provide a settable mixture is delivered in a separate stream. To blend the streams in the air space beyond each applicator conduit's exit opening, they can be pumped through nozzles that are aimed to cause the streams to collide in the air. Alternatively, the streams can be blended in a mixing head.

One advantage in not forming a settable mixture until all of the necessary ingredients enter or exit the applicator nozzle is that if the process has to be shut down early, there will be no volume of premixed resin in a supply vessel that will have to be discarded due to its having too short a pot life.

Once the process is past its start-up phase, the strips of cloth and web material can all be simultaneously and uniformly pulled through the continuous molder by grasping the emerging rigid composite and propelling it away from the molder, in the axial direction, e.g., by use of a tractor mechanism. The composite

-31-

can then be cut into desired lengths at a cutting station, e.g., by use of a flying cutter.

Once the process is past its start-up phase and the emerging composite is being pulled away from the continuous molder and thrust forward to the cutting station, tension can be placed on the cloth strips entering the continuous molder, so that the cords that make up the warp of the cloth (the lengthwise cords) are pretensioned when they are bonded to the matrix resin and the web material.

When using a foamable matrix resin, the specific gravity of the structural material that exits the continuous molder is controlled to some extent by the rate of deposit of the mixture of matrix resin precursor composition and filler solid on the moving web material. The greater the amount of mixture that is deposited per each foot of the moving web material, the more compressed will be the finished core material and, therefore, the greater will be its specific gravity.

If a thermoplastic matrix resin is used, the mixture of resin and filler solid has to be heated to a resin melting temperature either prior to deposition on the web material or after such deposition. Also, the last segment of the continuous molder may be equipped with cooling means, so as to cause the matrix resin to resolidify prior to the emergence of the composite material from the exit end of the die.

Even if a thermosetting matrix resin is used, there may be some advantage in cooling the last segment of the continuous molder so as to lower the temperature of the composite material before it exits the molder -- namely, by cooling it in the continuous molder the composite will undergo less deformation and its temperature will more quickly drop into a range in which the composite can safely be handled. Using tractor molds this requires a series of at least two such molds, so that the last tractor mold can be operated at a lower temperature than the mold in which the thermosetting occurs.

If heat needs to be applied to the mixture of matrix resin and filler solid while it is being carried through the continuous molder, any suitable source thereof

can be used, including, for example, radio frequency, microwave, and induction heating.

MAKING THE COMPOSITE STRUCTURAL MATERIAL WITH A ONE-PIECE COVERING

5 Alternatively, the composite structural material of the present invention can be made by use of nonwoven strands of reinforcing cord, and in such a way that the laminar covering is in one piece, rather than in two longitudinal sections. Thus, for example, a single strip of web material that is wide enough to completely ensheathe the core material, preferably with some overlapping, can be used.

10 Parallel strands of reinforcing cords, each from its own supply spool, can be laid on a side of the web material, the fluid mixture of matrix resin precursor composition and pieces of filler solid can be deposited on the cord-carrying side of the web material, and the web material can be forced into a sleeve-like configuration having the desired cross-sectional shape of the structural material, with the cord-carrying side facing the interior of the configuration. Then the mixture-carrying web material, while in the sleeve-like configuration, can be passed through the continuous molder as described above. In this embodiment the cords also can be pretensioned, once finished composite material is being pulled away from the molder. The porous web material can be sufficiently impregnated with stiffening resin precursor mixture that the reinforcing cords will not need to be independently wetted with bonding resin. Independent wetting of the cords still remains an option, however.

25 Preferably the web material is forced into its sleeve-like configuration prior to the mixture of matrix resin precursor composition and filler solid particles being deposited on the web material. The forcing of the web material into a sleeve-like configuration can be facilitated by wrapping the material around, and pulling it over, an elongated mandrel that corresponds in shape to the external die segments of the continuous molder. In this manner the mandrel imparts its shape to the web material and the external die helps to hold that shape.

-33-

Since it is preferred to force the web material into its sleeve-like configuration prior to depositing the resin/filler solid mixture on the web material, it is advantageous to use a mandrel that has an interior passage ending in an exit opening that is poised above the moving strip of web material. In that way, the mixture of resin and filler solid can be pumped through the mandrel's interior passage and out the exit opening, so as to be deposited on the web material. In this arrangement (as in the C channel embodiment) the web material acts like a tubular conveyor belt as it carries the mixture of matrix resin and filler solid through the continuous molder.

This process can also be performed using one or more strips of cloth, instead of individual strands of cord.

Yet another method of making an elongated version of the composite structural material with a one-piece covering is by the following steps:

- a) forming a foldable laminate of two strips of porous web material selected from the group consisting of paper and cloth, with at least one strip of cloth sandwiched therebetween, with the warp of the cloth running in the lengthwise direction and with the strips of porous web material and all materials lying between those strips being impregnated with a thermosetting resin precursor mixture;
- b) folding the laminate into a trough shape and orienting it horizontally, with one of the strips of porous web material on the top and the other strip of porous web material on the bottom;
- c) depositing in the trough of the laminate, while still foldable, a fluid matrix resin precursor composition that is compatible with the resin precursor mixture in the laminate and which, when fully reacted, yields a thermoset matrix resin that is at least semi-rigid;
- d) folding closed and sealing shut the laminate so that it surrounds and defines a core space containing said matrix resin precursor composition; and

-34-

- e) holding the closed laminate and its contents in a mold under conditions conducive to the setting of both the thermosetting resin in the laminate and the matrix resin in the core space, for a time sufficient for both resins to set, whereby
5 (i) the laminate and the matrix resin are both made at least semi-rigid, (ii) the matrix resin, together with any filler solid it may contain, fills the core space, and (iii) the laminate and matrix resin are bonded together.

SHIPPING PALLETS

As mentioned above, the present invention is ideally suited for the manufacture of composite boards that can be used to construct shipping pallets.

10 Any type of shipping pallet that can be constructed of wooden boards or blocks can be made using one or more composite boards or blocks of the present invention.

As is well known in the art, such pallets typically have deck boards (arranged horizontally) and stringers (also sometimes called "runners" or "posts") arranged vertically under a top layer of deck boards. Use of a bottom deck is optional.

15 Stringer pallets typically contain both edge and center stringers. Sometimes a single center stringer is used; but other times two center stringers will be used, e.g., either touching one another or separated by about 6 to 20 inches to distribute the load evenly.

20 Instead of stringers, some pallets comprise blocks and connector boards, to which are nailed top and bottom deck boards.

All of the boards may be of various widths, lengths, and thicknesses. Typically, however, deck boards are 1 x 4s or 1 x 6s. Stringers are typically 2 x 4s or 3 x 4s. A typical block pallet might contain 6 outer blocks, 3 center blocks, 3 connector boards, 4 top deck boards that are approximately 1 x 4 x 40 inches, 5 top deck boards that are approximately 1 x 6 x 40 inches, 3 bottom deck boards that are approximately 1 x 6 x 37 inches, and 2 bottom deck boards that are approximately 1 x 6 x 40 inches.

25 A stringer pallet can be configured as a two-way pallet, wherein the stringers permit the entry of forktrucks from two opposite directions only.

-35-

Alternatively, the pallet can be configured as a four-way pallet, wherein the stringers are notched, or otherwise cut, to permit entry of forktines from all four directions.

The deck and bottom boards in a stringer pallet can be flush with the outer edge of the outer stringers, making for a "flush pallet," or the deck and/or bottom boards can be extended past the outer edge of the outer stringers, making for a "single-wing" or "double-wing" pallet. Also, the bottom boards can be completely omitted, making for a "single-deck" or "skid" pallet.

If desired, the deck and bottom boards can be configured such that their number, size, and placement are the same, top and bottom, making for a "reversible" pallet.

The deck board composites might, for example, have a core that contains about 10 to 15 vol.% of granulated tire rubber and about 40 to 50 vol.% expanded perlite.

The deck boards can also be made without any filler solids in the core material, as they do not usually have to be dense enough to tightly hold a nail. E.g., they might be made with a core material consisting of polyurethane foam having a density of about 15 to 21 pounds per cubic foot (pcf), preferably about 17 to 19 pcf.

The deck-support boards preferably will contain at least some amount of granulated tire rubber, e.g., about 45 to 75 vol.%, most especially about 55 to 65 vol.%.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of one method of making a board-shaped composite material of the present invention.

Figure 2 is an elevation view of a shipping pallet constructed of boards of the present invention.

Figures 3 and 4 provide a schematic representation of another method of making a board-shaped composite of the present invention.

ILLUSTRATED PROCESS EXAMPLE 1

The invention perhaps will be better understood by considering the following description of one way of manufacturing the new composite structural material.

This example describes the construction of a composite board having the cross-sectional dimensions of a 1x4, i.e., 3/4 inch by 3-1/2 inches, using the C-channel method. The process is continuous and is illustrated schematically in Figure 1. The proportions in Figure 1 are not to actual scale. For example, for ease of illustration the thickness of papers 10 and 21 is exaggerated. So is the diameter of the warp cords 19 and the woof cords 20. And whereas the drawings depict approximately two dozen warp cords across the width of a 1 x 4, in actual practice there would preferably be at least 70. Also, Figures 1B through 1J are on a larger scale than Figure 1A, for ease of illustrating certain details.

Referring to Figure 1, a strip of recycled kraft paper 10 is pulled off supply roll 11, passed around guide roller 50, tension roller 51, and guide roller 52, and then passed over spray bar 12 where it is sprayed with a freshly prepared mixture of epoxy resin and hardener components. The combination of guide rollers 50 and 52 and tension roller 51 helps provide a uniform delivery of paper 10, i.e., without jerking. The cellulosic fibers (not shown) in paper 10 are oriented in the lengthwise direction of the strip. Meanwhile, woven polyester cloth 14 is pulled off supply roll 15, passed around guide roller 53, tension roller 54, guide roller 55, and a second tension roller 17, and then passed over spray bar 16 where it is sprayed with the same epoxy resin mixture. The resin-impregnated cloth 14 is pulled to laminating station 18, where it is pressed against the wet underside of paper 10, to yield the configuration shown in Figure 1D. As shown in Figures 1C and 1D, the warp of cloth 14 consists of cords 19. Cords 19 are held in place by woof cording 20, which is smaller in diameter.

A second strip of recycled kraft paper 21, identical to paper 10, is pulled from supply roll 22, passed around guide roller 56, tension roller 57, and guide

-37-

roller 58, and then is impregnated with the same epoxy resin composition, which is sprayed onto the upperside of paper 21 from spray bar 23. Meanwhile, polyester cloth 25 is pulled off its supply roll 26, passed around guide roller 59, tension roller 60, guide roller 61, and second tension roller 28, and then is sprayed on its underside with the same epoxy resin composition from spray bar 27. Cloth 25 is identical to cloth 14. Resin-impregnated cloth 25 is pulled into laminating station 29 where it is pressed against the inside bottom of paper 21, yielding the assembly illustrated in Figure 1E. At folding station 24 (equipment not shown) the edges of paper 21 are bent upward, creating an upward-facing C channel, as shown in Figure 1F. The combination of paper C channel 21 and polyester cloth strip 25 is pulled past ejection nozzle 30 where a mixture of matrix resin precursor components and filler solids is deposited on cloth strip 25. As shown in Figure 1G, the mixture deposit 31 consists of filler solids 32 suspended in a fluid mixture 33 of the components that will react to form a rigid, thermoset, polymeric foam. The combination of C channel, cloth, and core material precursor mixture 31, as shown in Figure 1G, is then pulled toward continuous molder 37. Before that combination enters molder 37, however, the laminated strips of paper 10 and cloth 14 are guided by roller 34 into position above bottom C channel 21, as shown in Figure 1H. Then top paper 10 is bent at folding station 13 (equipment not shown) into a downward-facing C channel that overlaps upward facing C channel 21, as shown in Figure 1I. That assembly is then pulled through continuous molder 37, which is maintained at an optimum temperature for assisting the forming, foaming, and setting of the resin precursor fluid 33, to yield cellular matrix resin 38, as shown in Figure 1J, which is a cross-sectional representation of the finished board. The interior (not shown) of continuous molder 37 is, in effect, an external die that holds the assembly of paper, cloth, and core material mixture in the desired cross-sectional shape. Pressure that presses the paper and cloth against the interior wall of continuous molder 37 is generated by the hot gas that is causing the resin to foam.

The finished board 40 is continuously pulled out of continuous molder 37 by tractor device 41. Once board 40 begins to emerge from molder 37, tension is placed upon cloth 14 by adjustment of tension roller 17, and tension is placed upon cloth 25 by adjustment of tension roller 28. Continuous molder 37 is long enough that, before board 40 emerges from the molder, cords 19 in both the top cloth 14 and the bottom cloth 25 are strongly enough bonded to rigidified paper strips 10 and 21, as well as to the foamed matrix resin 38, that, once the board is cut into sections, the tension in cords 19 will not be sufficient to break those bonds. Top C channel 10 is bonded to lower C channel 21 by the set epoxy resin at their interfaces 42 and 43 where their side walls overlap.

10

ILLUSTRATED PROCESS EXAMPLE 2

15

Another process for making a composite board of the present invention is schematically illustrated in Figures 3 and 4. In Figure 3, two-ply paper 101, which has an internal barrier layer of poly(vinyl alcohol), is fed from roll 102 over guide roller 103 through an epoxy resin applicator 104, using known technology and equipment for manufacturing paper and plastic laminates. Polyester scrim 106 is taken off roll 107 and also is passed through epoxy resin applicator 104. At the same time, single-ply paper 108 is taken off roll 109 and also is passed through epoxy resin applicator 104. The liquid epoxy resin precursor composition 113 (hereinafter called "epoxy resin," for short) is delivered through supply nozzle 110 to the space between papers 101 and 108.

20

25

As depicted coming off roll 102, the underside ply of paper 101 might advantageously be thinner than the upperside ply. This is because the underside ply only needs to be thick enough to receive a finish coating, not to absorb enough epoxy resin to be tightly laminated to a cloth scrim.

After leaving epoxy resin applicator 104, papers 101 and 108 and scrim 106 pass downwardly between calendar rollers 105 and 106, forming an unset laminate 111. The span of time between the application of the resin and emergence of the laminate 111 from rollers 105 and 106 is short enough that little or no epoxy resin

-39-

bleeds through paper 108 during that interval. However, as a precaution, a gravure blade 112 rides against calendar 106 to scrape off any epoxy resin that does get transferred to that surface.

Scrim 106 is sufficiently porous that epoxy resin 113 is easily pressed through the scrim by calendars 105 and 106. The flexible laminate 111 passes over guide roller 114 and then weaves its way over and under the array of festoon rollers 115. The space between the upper and lower gangs of festoon rollers 115 is set by computer so that the time required for the laminate 111 to complete the trip through the array allows the epoxy resin to partially set, but not rigidify. Rollers 115 can optionally be heated to speed up the setting of the epoxy resin.

As shown in Figure 4, flexible laminate 111 next passes through adjustable web creaser 116, where it is scored with four fold lines (not shown) that will form the four edges of the finished board. The creased laminate 112 next passes through forming station 117, in which it goes past forming rollers and/or mandrels (not shown) to bend it into a J-like cross-sectional configuration 118, using two of the crease lines imparted by web creaser 116. Two remaining crease lines 119 and 120 are visible in the high vertical side of the cross-sectional J.

Next the J-shape laminate 118 passes through core filling station 121, in which a mixture of matrix resin precursor components and filler solids (not shown) is deposited in the trough section of laminate 118. The mixture consists of filler solids and a fluid mixture of the components that will react to form thermoset polyurethane foam. Known equipment such as a mezzanine-mounted gravity feed filler (not shown) may be used to deposit the mixture in the trough of the moving laminate. Ideally a splash guard will be used to prevent any of the deposited mixture from bouncing out of the laminate trough.

The mixture-carrying laminate 122 next is passed through closing station 123, in which laminate 122 is folded along crease lines 119 and 120, so that edge 124 lays against the near side of the closed laminate 125. Closing station 123 includes a bead glue laminator (not shown) that seals the composite closed at edge

-40-

124, using a high-strength, heat-setting, fast-setting adhesive -- for example, an adhesive of the type used in the corrugated paperboard industry, e.g., an epoxy or polyamide/polyurethane adhesive. For example, a bead line of the sealing adhesive can be applied to the outside of the upstanding vertical edge, and the downwardly descending top edge can be pressed against the adhesive. In a few seconds, the adhesive sets sufficiently that the mixture-carrying sleeve 125 can enter tractor molding station 126, where sleeve 125 is held tightly in heated mold segments (not shown) while the matrix resin foams and partially sets and the epoxy resin in the laminate becomes at least somewhat rigid. Tractor mold 126 preferably is sufficiently strong to withstand an internal sleeve pressure of up to about 10 psi from the foaming polyurethane mixture. The resultant, partly rigid composite 127 then passes through a less substantial continuous molder 128, for the purpose of holding the composite in the desired rectangular shape while the resins further set, thereby preventing any bulging due to internal gas pressure.

10 Continuous molder 128 might only need to withstand a foaming pressure of about 6 or 7 psi. Therefore it might be a belt type continuous molder, rather than the more expensive tractor mold.

15

The resultant rigid composite 129 is pulled by tractor mechanism 130 out of the second tractor mold 128 and is passed forward to a cutting station (not shown). If desired, composite 129 can first be passed through a coating station where it is sprayed with a finish coating (not shown).

20

Once the process of Figures 3 and 4 has passed the start-up phase and is yielding a rigid composite 129 that is being pulled by tractor mechanism 130, tension can be applied to scrim 106. Tension can also be applied to paper 101 and/or paper 108. Preferably, enough tension is applied to paper 101 to keep a smooth and even outer surface all around the finished composite 129. Generally, machine tension will be sufficient for this purpose.

25

As will be appreciated, the system shown in Figures 3 and 4 can be modified to allow for the use of more than 3 plies in the laminate. The finished

-41-

board's rigidity, flexibility, durability, weight, burn characteristics, etc., can be affected by layering the laminate with various materials and various configurations. The following five laminates are specifically contemplated, with P representing an interior layer of paper, P_o representing the outermost layer of paper, S representing a layer of scrim, and P_i representing the innermost layer of paper:

1. $P_o - S - P_i$
2. $P_o - S - S - P_i$
3. $P_o - S - P - S - P_i$
4. $P_o - P - S - S - P_i$
5. $P_o - P - S - P - S - P_i$

ILLUSTRATED SHIPPING PALLET EXAMPLE

For illustration purposes, Figure 2 is an elevation view of just one type of shipping pallet that can be constructed of composite boards of the present invention. It is comprised of an upper deck 210 and a lower deck 211 that are both constructed of 1 x 4s. The end stringers 212 and 213 are 3 x 4s, set on edge. The two center stringers 214 and 215 are both 2 x 4s, also set on edge. Now follows a description of how, for example, the deck boards and stringers may be formed of composite structural material of the present invention.

Each of the boards is made with one-piece laminated coverings, as described in Example 2 and Figures 3 and 4. The $P_o - S - S - P_i$ arrangement of paper and scrim plies is used. The scrim has a warp made of 1000 denier multifilament polyester cords and a woof made of 250 denier multifilament polyester cords. The warp density is 12 cords per lateral inch; the woof density is 6 cords per longitudinal inch. (Other cloth, e.g., a fiberglass scrim, can be substituted for the polyester scrim.) The warp side of the scrim is toward the outside in each board. The P_o layer in all the boards is 100% recycled two-ply kraft paper having a basis weight of about 90 lbs., and the P_i layer is 100% recycled standard linerboard paper (single ply) having a basis weight of about 90

-42-

lbs. The laminate is rigidified with a two-component epoxy resin, such as Product Code R 88-14B/H 88-14E from Copps Industries, Inc. In all of the boards, the warp cords are pretensioned to about 80-85% of their capacity.

In the top deck boards 210, the core material is made of a mixture of 25.55 parts by weight (pbw) of a polyurethane foam system, 5.06 pbw of Huntsman Chemical 5371 EPS beads, and 69.39 pbw of No. 4 tire granule (minus 10 mesh) which has been magnetically separated, without removal of tire cord fluff. The polyurethane system consists of Baydur 645B isocyanate and Baydur 645A polyol. The EPS beads are substantially fully expanded prior to being mixed with the other ingredients. This core material has a specific gravity in the range of about 9.6 to 10.2 lbs/ft³.

The bottom deck boards 211 all contain a core material made of the same ingredients as the core material of boards 210, but in this ratio: 21.26 pbw polyurethane foam system, 6.57 pbw EPS beads, and 72.17 pbw granulated rubber. The cores of the bottom deck boards 211 all have a specific gravity in the range of about 9.3 to 9.8 lbs/ft³, about 0.2 to 0.4 lbs/ft³ less than the specific gravity of the core material in the top deck boards 210. (Alternatively, although not shown, the bottom boards might have the same core material as the top boards, but be about 17 to 33% thinner than the top boards, since they do not have to carry as much of a load. As a third option, the top and bottom deck boards can, of course, be identical.)

The stringers 212-215 all contain a core material made of a mixture of 28.58 pbw of a polyurethane foam system and 71.42 pbw of a granulated rubber. The polyurethane foam system consists of Baydur 645B isocyanate and Baydur 649A polyol. The same granulated rubber is used as in the deck boards. Due to the increased concentration of granulated rubber and the absence of any EPS beads, the core material of the stringers 212-215 has a specific gravity in the range of about 47.7 to 48.3 lbs/ft³.

All the deck boards (top and bottom) are held to the stringers 212-215 by Halstead gun nails No. HOR30131 and/or Halstead bulk nails No. BOT 30131,

-43-

both of which are high-grip, combination sink shank/drive screw nails having the following specifications:

- round, 0.295 to 0.305 inch diameter head
- head thickness of 0.065 - 0.070 inch
- countersink angle of 130°
- 3 inches in length
- ring shank width of 0.130 - 0.132 inch
- made from 0.120 inch diameter drawn, low carbon, steel wire
- diamond point with 42° angle
- minimum tensile strength (bend yield) of 100,000 psi
- coated with thermoplastic resin (a dried latex adhesive)

Although specific embodiments of the present invention have been described above in detail, it will be understood that this description is merely for purposes of illustration. Various modifications of and equivalent structures corresponding to the disclosed aspects of the preferred embodiments described above may be made by those skilled in the art without departing from the spirit of the present invention, which is defined by the following claims.